



Separations & Actinide Science

NEWSLETTER

JUNE 2009

CONTENTS

Quarterly Update on Separations and Actinide Science

Mike McIlwain

Synthesis, Characterization, and Testing of Dithiophosphinic Acid Derivatives

John Klaehn, Dean Peterman, Mason Harrup

New Radiological Measurements Laboratory Completed

Keith Arterburn

Upcoming Meetings and Symposia

Recent Publications



Tom Lints, left, and Gary Huestis, right, extract tritium from water samples in the new Radioanalytical Measurements Laboratory (RML), Building 678, located at the Advanced Test Reactor Complex.

Quarterly Update on Separations and Actinide Science

BY MIKE MCILWAIN
DISTINCTIVE SIGNATURE LEAD

During the second quarter, a number of significant developments occurred. These will have a positive impact on the Separations and Actinide Science activities at INL and across the DOE complex.

Here is a summary to keep you informed.

Budget, Looking to the Future

The Obama Administration is making progress in installing appointees. Most of the DOE assistant secretaries have been identified and are working their way through the congressional approval process. In fact, on June 10, Warren F. "Pete"

Miller was named as the likely nominee as Assistant Secretary for Nuclear Energy.

More importantly, the FY2010 Presidential budget was released and proposed a sizable increase in expenditures for physical sciences. As a consequence of the Yucca Mountain closure decision, the Advanced Fuel Cycle Initiative (AFCI) budget was increased dramatically. The separations science and engineering component of this program also enjoyed a substantial increase. Should Congress appropriate these increased budgets, the separations research activities at INL and across DOE should be greatly enhanced. While funding opportunities for actinide science related research have been abundant, INL still struggles in obtaining Office of Science funding. However, INL's actinide science research efforts are receiving more and more recognition for exceptional high quality presentations and publications.

Actinide Separations Conference

INL was well represented at the recent Actinide Separations Conference held in Reno, California in May. More than 70 national laboratory and academic researchers gathered to discuss recent research and operational developments. INL's Terry Todd, Ph. D., INL Fellow and AFCI separations campaign leader, gave an informative and comprehensive plenary presentation on future programmatic directions in the AFCI program. The technical session portion of

the meeting provided an excellent opportunity to collect information related to separation research at other laboratories.

New INL Facilities

During this quarter, good news was announced related to significantly expanded radiochemistry laboratory space associated with the approval of the Research and Education Laboratory (see the conceptual design of the new facility on page 7). This 50,000 square-foot building will be located adjacent to the Engineering Research Office Building. It will provide more than 7,000 square feet of modern radiochemistry space and an additional 7,000 square feet for analytical and synthetic chemistry work, when the facility is completed in 18 to 24 months. A new Radiological Measurements Laboratory was recently brought on line at the Advance Test Reactor complex and is highlighted later in this newsletter.

These good things are strengthening the Separations and Actinide Science Signature related research activities and improving laboratory facilities and capabilities.

Synthesis, Characterization, and Testing of Dithiophosphinic Acid Derivatives

Laboratory Directed Research and Development Project Number C.B.10.00.GL.01.04

BY PRINCIPAL INVESTIGATOR JOHN R. KLAHN, AND CO-INVESTIGATORS DEAN R. PETERMAN AND MASON K. HARRUP

Technical Approach

A currently studied extractant for the separation of actinides from nuclear waste streams is an aliphatic dithiophosphinic acid (DTPAH) derivative, Cyanex® 301 [bis(2,4,4-trimethylpentyl)-dithiophosphinic acid]. While extraction conditions have been well established to maximize the effectiveness of this extractant, this ligand can be improved. It would be advantageous if the ligand were more acidic, lowering the pH range where efficient extraction will occur. Also, increased stability of both radiolytic and chemical degradation would yield a better extractant. Fluoroaromatic derivatives of DTPAH were chosen for lowering the pKa, making the sulfhydro proton more acidic.

The electron-withdrawing properties of these species are well known for increasing the DTPAH acidity. In addition, it has been shown that aromatic DTPAH compounds can be stable towards both chemical degradation (nitric acid) and radiolytic environments. Therefore when designing DTPAH extractants, one should use similar aromatic attributes that should make the compound more robust under extraction conditions.

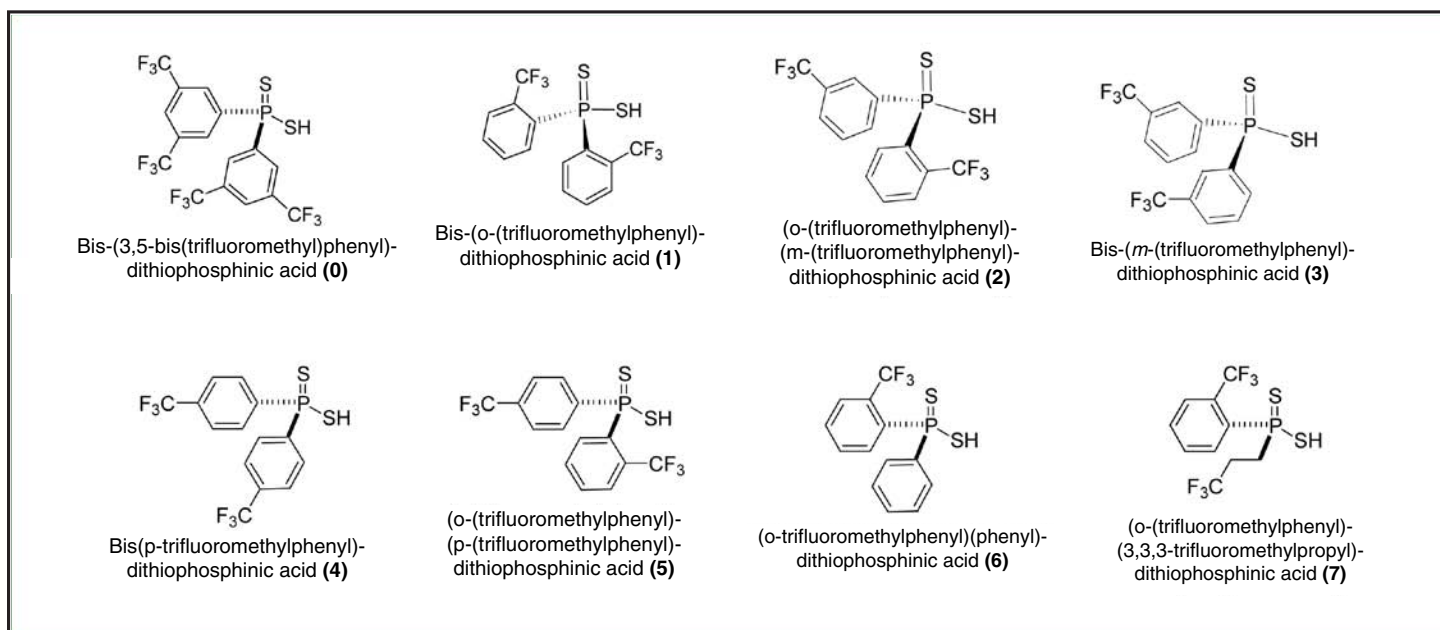


Figure 1. Synthesized Dithiophosphinic Acids (DTPAH).

The INL synthetic route offers several new organic pendant groups from the phosphorus core that are more electron-withdrawing than the simple aliphatic pendant groups present in Cyanex® 301. In stark contrast to all prior research, INL's route offers two key advantages. Isolation of a single DTPAH product that is regiospecific, and the synthesis is able to produce novel asymmetric products (two different functional groups on phosphorus).

Technical Objectives

The technical objectives of this research to develop advanced extractants are to:

- Synthesize and characterize various derivatives of dithiophosphinic acid core,
- Analyze the stability of these molecules towards acidic, aqueous media, and
- Evaluate these compounds for the separation of actinides

from lanthanides via batch contacts.

Results and Accomplishments

The synthetic route has been successfully proven at INL with various DTPAH derivatives; both symmetric and asymmetric (Figure 1). The synthesis has been improved by isolating the DTPAH derivatives as the ammonium salts and then converting them into the corresponding acids.

Overall, the yields and purity for all of the shown DTPAH compounds are improved relative to the previous isolation methods. This accomplishment provides support for the view that the synthetic pathway could be scaled-up for commercial-scale production of these DTPAH derivatives.

This year, compounds (4), (5), and (6) were successfully isolated

as the ammonium salts, and these products are all new DTPAHs. This accomplishment completes the series of the various aromatic isomers of DTPAH compounds (0-7) (Figure 1), and this series will provide a better understanding how the trifluoromethyl group position influences lanthanide(III)/actinide(III) [Ln(III)/An(III)] selectivities.

Compound (4) has been synthesized previously; however, it was never isolated due to rapid oxidation during workup procedures. Changing synthetic protocol afforded (4) to be isolated in good yields. In addition, (5) was isolated with minor complications due to a small amount of (4) that was isolated.

The synthesis of (7) was to provide a theory that the same proximity of the trifluoromethyl group would still provide good separations; however (7) was not successfully

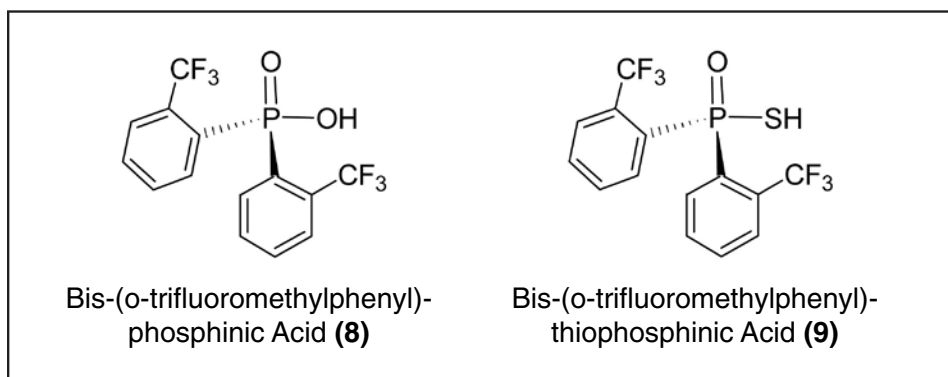


Figure 2. Phosphinic Acid (**8**) and Thiophosphinic Acid (**9**).

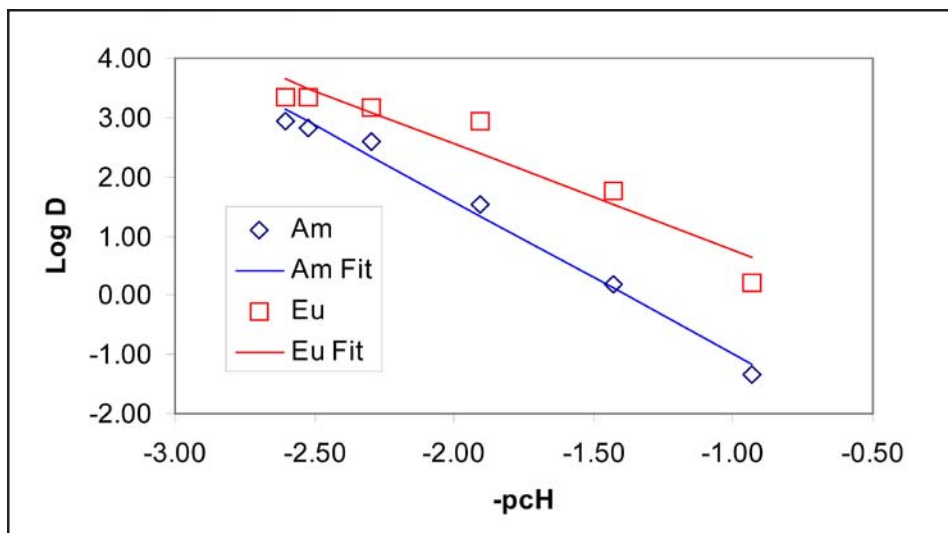


Figure 3. Phosphinic acid (**8**) Distribution Ratios of Am(III)/Eu(III).

isolated. It was postulated that (7)'s short propyl chain does not allow the ammonium salt of (7) to precipitate properly and this resulted in a mixture of phosphorus products that could not be separated.

Also this year, the analogs of (1), dioxo (**8**) and thio-oxo (**9**), were synthesized (Figure 2). The premise for synthesizing these compounds was to determine whether the ligand structure of (1) could confer a preferential affinity towards Am³⁺ with harder donor atoms. A new synthetic route was used for the synthesis of (**8**) and it

was successfully isolated. Using a similar synthetic route did not yield (**9**), due to rapid oxidation of the phosphorus center.

All of the other DTPAH compounds have been analyzed by multinuclear NMR, and X-ray structural determination was used for some of these compounds. One particularly interesting feature of the X-ray structures is the position of the o-trifluoromethylphenyl groups (o-CF₃) on (1). These o-CF₃ groups for both the ammonium salt and the free acid form of (1) are in close proximity to

the back of the phosphorus atom in the solid state. This interaction between the fluorine and phosphorus orbitals could be providing for some form of back-bonding. There is some speculation that there exists through-space interaction between the phosphorus center and the o-CF₃ groups, which may aid in the explanation of the observed Ln(III)/An(III) separation efficiency. Further, the steric proximity of these o-CF₃ groups to the phosphorus center may also explain the increased stability that has been observed.

This year, some of the isolated DT-PAH derivatives (see Figures 1 and 2) were tested for the separation efficiency using actual radioactive actinide(III)/lanthanide(III) extractions. Several different tests have been performed to describe the overall behaviors of the DTPAH using extraction conditions that simulate actual use.

The results of these laboratory studies indicate that the extractant exhibits significantly better performance in terms of the separation efficiency and extractant stability compared to currently available actinide/lanthanide selective extractants. When dissolved in a suitable organic diluent, the new extractant is able to separate Am(III) from Eu(III) [americium(III) from europium(III)] in aqueous solutions containing significant concentrations of nitric acid.

Laboratory tests have utilized 0.1M solutions of DTPAH dissolved

in trifluoromethylphenylsulfone (FS-13) as the organic solvent. The aqueous phase consisted of tracer concentrations of ^{241}Am and ^{154}Eu . The supporting species in the aqueous phase was 1.00mM stable Eu (III) in a supporting electrolyte of 1.00M NO_3^- with the counter cation consisting of a mix of H^+ and Na^+ to maintain the aqueous phase acidity at the desired values.

This year, a calibrated pH meter was used to experimentally determine the corrected pH (pCH) of the aqueous phase after each extraction experiment. The distribution ratios were determined via standard gamma spectroscopy techniques and are reported as $D = [\text{organic}]/[\text{aqueous}]$ after contact and phase separation.

The extraction data obtained on DTPAH compounds (0-3) showed significant separation at pH values greater than 2.5; however, (4-5) show minimal extraction behavior at pH values 1-4. Compound (0) did not separate Am from Eu with an extraction efficiency of only ~20. Conversely, (1) [two o- CF_3 groups] and (2) [one o- CF_3 group and one meta- CF_3 group] provided the most effective separation of ~100,000 for one batch extraction.

When both of the CF_3 groups were in the meta positions (3), the effective separation was reduced nearly two orders of magnitude less than (1) and (2) to about 1000. Interestingly, placing both of the CF_3 groups in the para positions, (4)

gave no effective separation. It is believed that the electron withdrawing effects of the CF_3 groups dominate and make the sulfur atoms on (4) less electron rich leading to poor Am(III)/Eu(III) selectivities.

However, changing the DTPAH to one phenyl group and an o- CF_3 phenyl group, (6) afforded minimal effective separation. The Am(III) distribution ratios for (6) were less than one, but the Eu(III) distribution ratios were still much less than one. This shows that an additional o- CF_3 group is needed to give the correct electronic effects for effective separation, like compounds (1) and (2).

Finally, the phosphinic acid (8) was tested using the same extraction conditions as the previous DTPAHs (Figure 3). Notably, (8)'s distribution ratios (D) for Am(III) and Eu(III) shows reverse selectivity towards Eu(III) over Am(III) (~10). Therefore, the replacement of the softer sulfur donors with oxygen donors leads to a decrease in actinide/lanthanide selectivity and effectively removes Eu(III) from the aqueous phase at low pH (~1).

Overall, the separation factor differences among the synthesized DTPAH compounds (0-4, 6) were fairly dramatic. Our present data suggests that the o- CF_3 group will give an enhanced separation using our current extraction conditions. This was shown for (1) and (2), which gave separations superior to (0, 3, 4, 6). These tests confirmed that (1) and (2) were superior extractants to any alternatives available.

Conclusions

We conclude that the INL synthetic route can be expanded to produce other new phosphinic acid derivatives, in particular the asymmetric DTPAH and PAH derivatives.

Our isolated products, (1) and (2), are great alternatives to Cyanex® 301. It should be noted that these DTPAH compounds can extract Am(III) under acidic environments (pH = 2.5), where Cyanex® 301 does not function effectively. Notably, (8) could be used for Eu(III) over Am(III) separations at much higher pH, but the effective separation is low. Overall, INL has provided a successful synthetic route, which includes compounds (1) and (2) that gave effective separation greater than 80,000 using the current extraction conditions!

New Radiological Measurements Laboratory Completed

BY KEITH ARTERBURN

Just in time for 'Tax Day,' April 15, the Radiological Measurements organization occupied a new laboratory space, Building 678, located in the neighborhood at the Advanced Test Reactor (ATR) Complex.

"The new Radiological Measurements Laboratory (RML) adds more new laboratory space to support INL's nuclear mission," said Mike McIlwain, lead for the Actinide Science and Separations Signature and department manager for Interfacial Chemistry.

“This new laboratory, along with several other new spaces, advances progress toward our strategic plan focused on transforming the ATR into the hub for the nation’s nuclear research,” he added.

This move marked the completion of the second of three phases needed to relocate research and operations support activities being conducted in the MTR-604 laboratory facility.

Originally constructed in the 1950’s, MRT-604 was not maintained, required substantial facility upgrades, and identified for decommissioning and demolition.

The first phase of the relocation process moved most of the radioanalytical chemistry and radiochemical research activities to other facilities, including CFA 625 and Hot Fuel Examination Facility (HFEF) laboratories. These moves were completed in January 2009, after some modifications to existing facilities. The activities being conducted at CFA 625 and HFEF will be the subject of future newsletter features.

Since it was necessary to maintain radiological measurement support adjacent to the ATR, phase two of the relocation process necessitated substantial modifications to building 678 at the ATR Complex (Photo 1), including internal walls that provided separate instrumentation rooms (Photo 2), a wet chemical laboratory (Photo 3), and

Photo 1. The new RML (Building 678) at the ATR Complex, was completed in April 2009. Concrete barriers, at right side, provide shielding from the MTR reactor vessel removal activities.



Photo 2. The counting laboratory within the RML has four gamma ray measurement stations.



Photo 3. The tritium radiochemical laboratory inside the RML has three HEPA filter chemical fume hoods.



Photo 4. The iron room measurement laboratory is used for determination of low energy gamma ray emitting isotopes.



Photo 5. The site for a new Radioanalytical Laboratory within the ATR Complex is adjacent to a recently constructed office building, in the background.



a sample management office. An addition to the building created space for a shielded instrumentation laboratory, staff offices and two steel shielded, low background measurement areas (Photo 4). The third phase will construct a new radiolanalytical chemistry laboratory, adjacent to the new office building at the ATR Complex.

Construction of this new laboratory began in May 2009 with completion scheduled for some time early in 2010. Site preparation activities have begun with the pouring of the facility foundations (Photo 5). This new laboratory will add about 5,000 square feet of research space with six to nine HEPA filtered chemical fume hoods and several

large instrumentation laboratories. When the construction activities are completed, radiochemical activities currently being performed at CFA 625 will be relocated to the new facilities. As a result, the ATR will again have radiochemical support for operations and experiments, as well as tritium measurement support to the Star Facility.



This conceptual drawing illustrates what the new Research and Education Laboratory might look like. The 50,000 square foot building will be located next to the Engineering Research Office Building, and will provide more than 7,000 square feet of radiochemistry space—and an additional 7,000 square feet for analytical and synthetic chemistry research. The building is expected to be completed in about 24 months.

Actinides 2009

July 12-17, 2009; San Francisco, CA

238th ACS National Meeting

August 16-20, 2009; Nuclear Energy and the Environment Session; Washington, DC

The Seventh International Conference on Nuclear and Radiochemistry (NRC-7)

August 24-29, 2009; Budapest, Hungary

APSCORC'09—4th Asia-Pacific Symposium on Radiochemistry

November 29 to December 4, 2009; Napa, CA

Materials Research Society Symposium on “Scientific Basis for Nuclear Power”

December 1-5, 2009; Boston, MA

RECENT PRESENTATIONS AND PUBLICATIONS

Meikrantz, D., Tranter, T., Tillotson, R., Horwitz, P., and Harvey, J., “Recovery of Ac225 from Aged Light Water Breeder Reactor Fuel”; 33rd Actinide Separations Conference; Reno, CA, May 2009.

Groenewold, G.S., “Spectroscopy of Small Molecules: IR Studies of Discrete f-Element Complexes” Very Heavy Metals 2009; Canet, France, May 27 to June 1, 2009.

McJunkin, T.R. and Scott, J.R., “FT-ICR-MS Cell with Linear Excitation/Detection and No Net Magnetron Motion;” ACS 237th American Chemical Society National Meeting and Exposition; Salt Lake City, UT, March 22-27, 2009.